



A facile route for PbO@C nanocomposites: An electrode candidate for lead-acid batteries with enhanced capacitance

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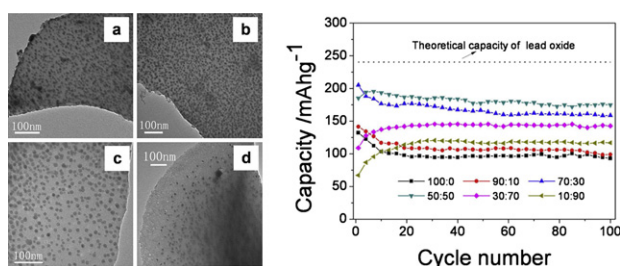
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HIGHLIGHTS

- ▶ PbO@C nanocomposites were prepared by pyrolyzing Pb(NO₃)₂ impregnated starch gel.
- ▶ Monodispersed PbO nanoparticles were homogeneously embedded in the carbon matrix.
- ▶ PbO@C nanocomposites prepared exhibited the capacity of 205 mA h g⁻¹.
- ▶ Products prepared were promising electrode candidates for lead acid batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel and facile synthetic approach is developed to prepare the PbO@C nanocomposites by using starch as the carbon precursors. Nearly monodispersive lead oxide nanoparticles embedded carbon nanocomposites are produced via pyrolyzing Pb(NO₃)₂ impregnated starch gel under the N₂ atmosphere at 700 °C. The PbO nanoparticles are ca. 10 nm in size and slightly changed with the [Pb(NO₃)₂]:starch] ratios varied. XRD patterns and XPS data reveal the presence of α -PbO, orthorhombic β -PbO and Pb in the nanocomposites without any tetravalent Pb⁴⁺ species. When used as anode materials for the lead-acid battery, the nanocomposites exhibit an improved performance. PbO@C nanocomposites prepared from the mixtures with [Pb(NO₃)₂]:starch] of 70:30, 50:50 and 30:70 exhibited the highest capacity of 205 mA h g⁻¹, the highest residual capacity of 185 mA h g⁻¹ and the best cyclic stability after 100 charge/discharge cycles, respectively.

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1. Introduction

Global concern has focused on sustainable and renewable power resources as well as energy storage systems. Although much attention is presently paid to the Li-ion battery, lead-acid battery is

still the most widely used rechargeable energy storage system and occupies a large market share of the rechargeable battery due to its advantages, including the low processing cost, simplicity of design, reliability and relative safety [1–3]. However, lead-acid battery is limited in the low-energy capacitance and cycling stability compared with other electrochemical systems and hard to meet the demands of storing the power from the sun and wind. Also, it is difficult to fit the requirements of electric vehicles as an alternative to fossil fuels. The widely used uninterruptible power system (UPS) and emergency power supply (EPS) also need improve the specific

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energy and the cycling stability. Designing cost-efficient, light-weight and effective electrode materials has become an increasingly imperative to improve the performances of lead-acid battery such as the high power and discharge rates, a long cycle life and a substantial weight reduction [4–6].

Recent studies indicated that the morphologies and sizes of electrode ingredients played an important role on enhancing the electrochemical activity of the electrode [7–11]. Some groups attempted to improve the discharge capacity, the specific energy and the cycling stability by reducing the electrode particle sizes of lead oxide and lead dioxide into nanoscale [12–14]. Although much work has been done on the preparation of the nano-structured lead oxides, few focused on the structure-dependant electrochemical properties. The documented methods for lead oxides nanostructures, such as electrodeposition [8,15], spray pyrolysis [4,12,16], sonochemical [17,18] and hydrothermal [19–21] approaches, is generally limited to the complex procedure, low productivity, time-consuming and sometimes poor reproducibility. As well, it was hard to get the composites by these routine methods.

On the other hand, carbon-based nanocomposites of metal or metal oxides have been widely used as the catalysts in fuel cell and other battery systems [22–24]. Recent results also implied that compositing carbon with PbO_2 or PbO would improve the battery performances and decrease the weight of electrode, so that this behavior is beneficial to protect from the lead pollution. These materials had exhibited interesting properties when used as the electrodes in Li-ion battery with the enhanced properties in the documents [17,18,25,26]. However, preparing the well dispersed carbon nanocomposites is still a paramount challenge at present [27–29]. Conventionally, the carbon-based nanocomposites were prepared by heating the metal cation or anion impregnated carbon. This method is generally limited by the large average particle sizes, agglomeration of nanoparticles, broad size distribution, and poor reproducibility. If metal species were highly dispersed in the carbon precursors, controlled heat treatment may produce the well-dispersed metal or metal oxide nanoparticles in the carbon substrate. Starch has been widely used as a carbon resource because of its low-cost and easy accessibility [30,31]. Furthermore, starch molecules are soluble in water and abundant in the hydroxyl groups on their carbon chains. These hydroxyl groups are readily coordinated to metal cations in the solution to generate a homogeneous mixture in the molecular level. Controlling the heat treatment will produce high quality carbon based nanocomposites. Herein, a facile method was developed for fabricating PbO@C nanocomposites by carbonizing $\text{Pb}(\text{NO}_3)_2$ impregnated starch gel under the nitrogen (N_2) atmosphere at a moderate temperature ($<1000^\circ\text{C}$). Electrochemical test revealed that the as-prepared materials were promising electrode candidates for lead-acid battery with increased specific capacity.

2. Experimental

2.1. Synthesis of PbO@C nanocomposites

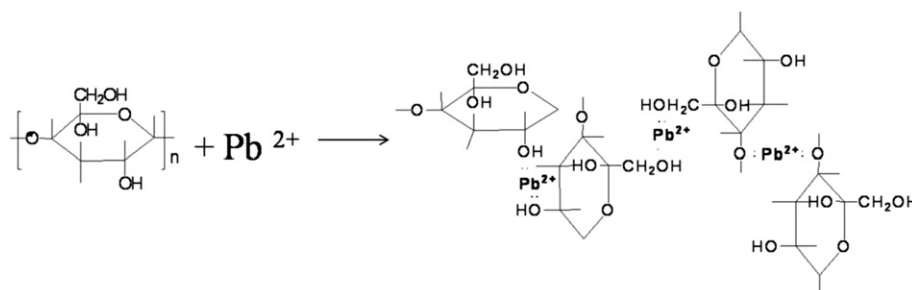
PbO@C nanocomposites were prepared by carbonizing $\text{Pb}(\text{NO}_3)_2$ impregnated starch at high temperature. Starch was an industrial product and readily available elsewhere. All chemicals were used as received. Typically, the $\text{Pb}(\text{NO}_3)_2$ impregnated starch gels were prepared by mixing lead nitrate and starch in water under stirring with various $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$ weight ratios of 100:0, 90:10, 30:70, 50:50, 40:60, 30:70 and 10:90, respectively. During the process, the oxygen-rich group in the surface of starch probably organizes the nanostructures by forming cation–starch complex (Scheme 1). The starting gels were aged and dried in the vacuum oven at 60°C . Afterward, the gels were calcined under the N_2 flow in a tubular furnace at 700°C for 3.5 h ($10^\circ\text{C min}^{-1}$).

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Discover instrument with a CCD detector operating at 40 kV and 20 mA, by using $\text{CuK}\alpha$ radiation ($\lambda = 0.15406\text{ nm}$). Transmission electron micrographs (TEM) of samples were taken on a Hitachi H-7650 microscope with an accelerate volt of 80 kV. The samples for TEM observations were prepared by dipping ethanol suspensions of finely grounded nanocomposites onto the copper grids. The size distributions of the PbO particles were evaluated by the TEM images. 2–500 particles were measured for each sample to obtain statistically significant results. The loadings of PbO into the carbon matrix were determined by thermogravimetric analysis (TGA), which was performed on a Netzsch STA 409 PG/PC under an air flow with a heating rate of $10^\circ\text{C min}^{-1}$. X-ray photoelectron spectroscopy (XPS) of the nanocomposites was recorded using a ThermoFisher K-alpha X-ray photoelectron spectroscopy employing a monochromated $\text{Al-K}\alpha$ X-ray source ($h\nu = 1486.6\text{ eV}$), survey spectra were recorded with a pass energy of 200 eV, and high resolution spectra with a pass energy of 50 eV.

2.3. Electrochemistry measurements

Cyclic voltammetry was carried out at the room temperature on a CHI 660C electrochemical workstation (Shanghai Chenhua Apparatus Co. Ltd) at a scanning rate of 50 mV s^{-1} . A conventional three-electrode electrochemical cell was employed in the measurements. An Ag/AgCl within the saturated KCl solution was used as the reference electrode and Pt gauze as the counter electrode. The anode was made from the PbO@C nanocomposites by using the acetylene black as the conductive reagent and the polytetrafluoroethylene (PTFE) as the binder. At first, a paste was prepared by mixing 85 wt.% as-prepared PbO@C nanocomposites,



Scheme 1. The schematic illustration of the interaction between Pb^{2+} and starch molecules.

10 wt.% acetylene black and 5 wt.% PTFE (60 wt.% solution). The mixtures were ground for 20 min to obtain a homogeneous limber black solid. The final mixtures were packed into the cave of a Teflon tube (3 mm in diameter and 3 mm in depth). An electrical contact was built via a platinum wire (0.5 mm in diameter). The electrode was dried at 80 °C for 24 h. The cathode plate for the battery performance test was made according to the method in the literature [32]. The plate dimensions were 20 mm × 10 mm × 2.5 mm. The as-made anode and cathode were used for the battery test. The electrolyte was the H₂SO₄ solution with density of 1.24 g cm⁻³. The galvanostatic charge/discharge was conducted in the voltage range of 1.0–2.5 V on a Program Testing System (Wuhan Lixing Co. Ltd., China) at the current density of 200 mA g⁻¹, 400 mA g⁻¹, and 800 mA g⁻¹.

3. Results and discussion

3.1. Formation mechanism and composition of PbO@C nanocomposites

The PbO@C nanocomposites are synthesized by calcining Pb(NO₃)₂ impregnated starch gel at 700 °C in a N₂ flow for 2 h. As well known, starch molecules contain plenty of hydroxyl groups and serve as the multi-dentate ligands. These hydroxyl groups are readily coordinated to the metal cations in aqueous solution to produce homogeneously distributed metal starch complexes as shown in Scheme 1. When heated at the elevated temperature, small particles of the metal oxides will be formed in the carbon matrix. The starch molecules serve as both the carbon resources and the inhibitors to generate the large particles.

To determine the content of PbO and study the decomposition behavior of the PbO@C nanocomposites, TGA investigations were carried out at a heating rate of 10 °C min⁻¹ in an oxygen atmosphere (Fig. 1). Samples prepared from the pure Pb(NO₃)₂ and mixtures of 90Pb(NO₃)₂:10starch are very close and stable, indicating the pure inorganic features. The product from pure starch exhibits 90.1% weight loss up to 800 °C. The residual may be the graphitized carbon. TGA curves also disclose abrupt mass losses between 300 and 500 °C for the samples from starting mixtures with [Pb(NO₃)₂:starch] ratio of 70:30, 50:50, 40:60 and 30:70. The decomposition processes give the PbO contents of 99.9, 86.1, 84.6, 58.2, 44.7, 16.0 wt.% for the samples synthesized from the precursors with [Pb(NO₃)₂:starch] weight ratio of 90:10, 70:30, 50:50, 40:60, 30:70, 10:90, respectively (Table 1). The carbon contents were significantly below the theoretical value. As well-known, the

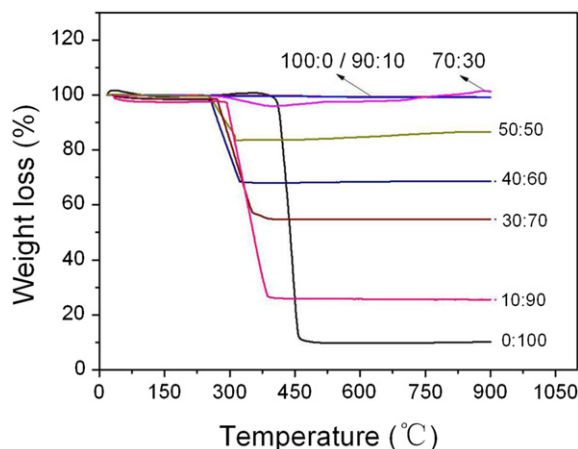


Fig. 1. TGA curves of nanocomposites prepared from different Pb(NO₃)₂:starch ratio.

Table 1

The composition of PbO@C nanocomposites prepared from various [Pb(NO₃)₂:starch] ratio.

[Pb(NO ₃) ₂ :starch] (wt.%)	Lead oxides (wt.%)	Lead oxides size (nm) ^a
90:10	99.9	Microparticles
70:30	86.1	24
50:50	84.6	9.0
40:60	58.2	11.4
30:70	44.7	13.5
10:90	16.0	12.4

^a Mean PbO size.

decomposition of Pb(NO₃)₂ will produce NO₂ and O₂. The excess of carbon losses stemmed from oxidizing the starch by NO₂ and O₂. When the content of starch was very low, all the starch would be converted into carbon dioxide due to the presence of NO₂ and O₂ byproducts. That means the low starch contents cannot afford composite materials in the present work.

3.2. Analysis of XRD patterns

The phase identification of lead oxide in the nanocomposites was completed by using the X-ray diffraction. The XRD patterns of samples prepared from mixtures with various mass ratios of [Pb(NO₃)₂:starch] are shown in Fig. 2. The lead oxide species in the nanocomposites are the mixtures of two phases, tetragonal α-PbO and orthorhombic β-PbO. No peaks of Pb₃O₄ and PbO₂ were obviously observed. The presence of carbon prevented the formation of tetravalent lead oxide. The diffraction peaks at 29.1°, 37.8°, 50.8° and 56.0° were observed in all the samples, which were assigned to the orthorhombic β-PbO (JCPDS card No. 05-0570) [12]. When the content of starch was lower than 50% in the starting mixture, the nanocomposites contain the mixtures of tetragonal α-PbO (JCPDS card No. 05-0561) [18] and orthorhombic β-PbO. The characteristic

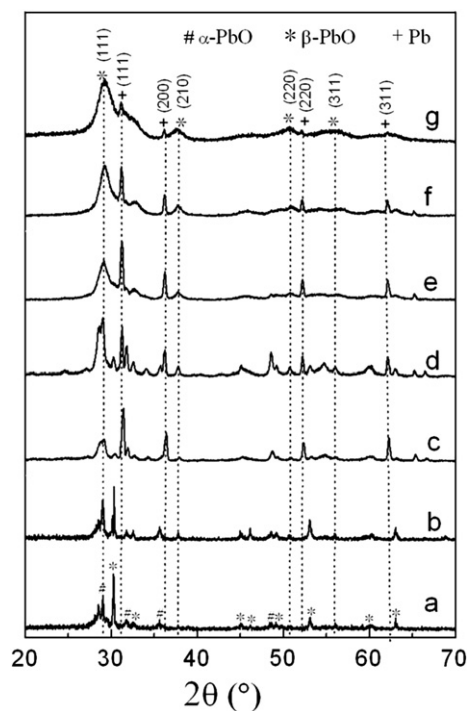


Fig. 2. XRD patterns of various PbO@C nanocomposites calcined at 700 °C with the initial weight ratio [Pb(NO₃)₂:starch]. (a) 100:0; (b) 90:10; (c) 70:30; (d) 50:50; (e) 40:60; (f) 30:70; (g) 10:90.

diffraction peaks of Pb (JCPDS card No.04-0686) [33] were detected in the samples from $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$ ratio of 70:30, 50:50, 40:60, 30:70, 10:90. As the carbon content increases, the peak intensity of the orthorhombic β -PbO phase enhanced significantly with the peak intensity of the tetragonal α -PbO phase reduces. No peaks of α -PbO were obviously observed when the starch content was over 60 wt.% in the starting mixtures. The excess of carbon was helpful to the formation of β -PbO. XRD patterns indicated that Pb formed when the starch content was larger than 30%. Increasing the carbon content also resulted in weakened and broadened diffraction peaks of both Pb and β -PbO (Fig. 2c–g). The widened peaks implied the small sizes of the lead oxides particles. The occurrence of Pb was originated from reducing PbO by excess of carbon. The absence of peaks of any crystalline carbon in the XRD patterns also disclosed the amorphous feature of the carbon substrate in the PbO@C nanocomposites.

3.3. Analysis of XPS spectra

Fig. 3 presents the survey XPS spectrum of PbO@C nanocomposites. Besides the C(1s) signal at 284.5 eV, O(1s) at 531.2 eV, and O(KLL) at 977 eV, the Pb(4f), Pb(4d3), and Pb(4d5) signals appeared in all samples. The Pb(4d5) signal at 412 eV reveals the presence of metallic Pb species in the composites, which is in agreement with the XRD data. Notice that as the carbon content increased the Pb signals gradually weakened with the C signals strengthened due to the augmentation of carbon content. The peaks of O1s at 531.2 eV ascribed to O1s of PbO. The shoulder peaks of O1s indicated the presence of C–O bond, which was due to a small amount of incomplete carbonized starch molecules.

Fig. 4 shows the Pb4f XPS spectrum of the sample from 50Pb(NO_3)₂:50starch. The peaks centered at 138.04 eV corresponded to the binding energy of Pb4f7, which was very close to the documented value of PbO (138.1 eV) [34]. 4.85 eV binding energy gap between Pb4f5 and Pb4f7 was a characteristic of PbO with the

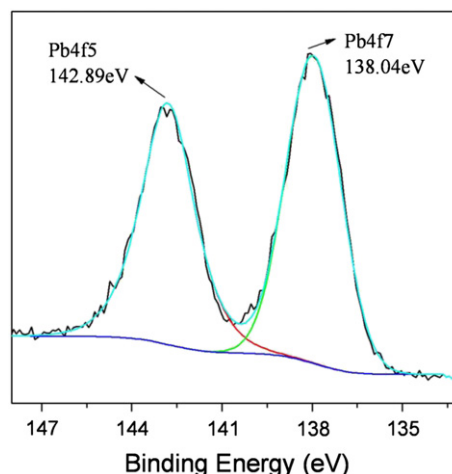


Fig. 4. XPS spectrum of Pb4f for the PbO@C nanocomposite from 50Pb(NO_3)₂:50starch.

area ratio of these two peaks of 4:3. The absence of peaks of tetravalent Pb^{4+} in the XPS results further confirmed that the nanocomposites only contained PbO and Pb in the nanocomposites. This result was consistent with that of XRD experiments.

3.4. Microstructural analysis by TEM

TEM was used to study the microstructure of PbO@C nanocomposites (Fig. 5). Samples from the pure $\text{Pb}(\text{NO}_3)_2$ and a starting mixture with $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$ ratio of 90:10 exhibited the similar morphologies with sub-micrometer sized irregular plate shapes (Fig. 5a and c). The product from pure starch (Fig. 5b) was the large blocks in shapes. The spherical PbO nanoparticles formed with a broad size distribution of 5–24 nm (Fig. 5d) when the $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$ ratio was adjusted to 30:70. A distinct contrast difference in the image suggested the

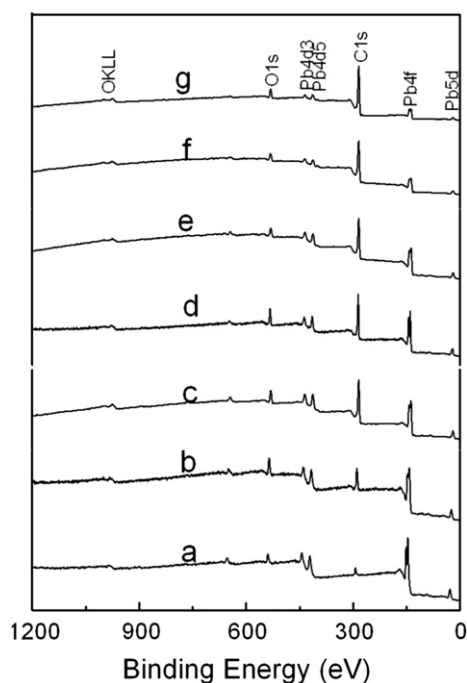


Fig. 3. XPS survey for various PbO@C nanocomposites calcined at 700 °C with the initial weight ratio $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$. (a) 100:0; (b) 90:10; (c) 70:30; (d) 50:50; (e) 40:60; (f) 30:70; (g) 10:90.

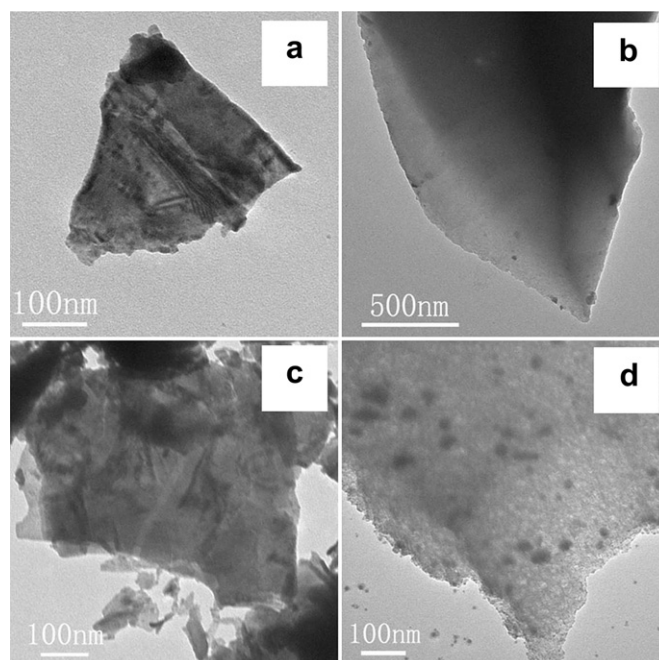


Fig. 5. TEM image of bare PbO (a) and bare carbon (b) and PbO@C nanocomposite calcined at 700 °C with the initial weight ratio $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$: (c) 90:10; (d) 70:30.

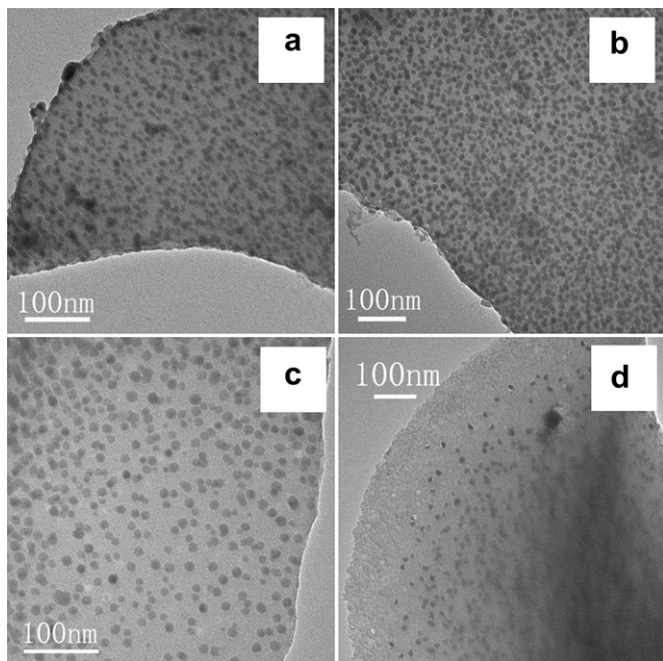


Fig. 6. TEM image of PbO@C nanocomposite calcined at 700 °C with the initial weight ratio $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$: (a) 50:50; (b) 40:60; (c) 30:70; (d) 10:90.

existence of amorphous carbon and the lead oxide phases. When the starch content was further increased in the starting mixture, heat treatment produced homogeneously embedded PbO nanoparticles in the carbon matrix (Fig. 6a–d). The TEM images clearly revealed that the small lead oxide nanoparticles greatly detached from each other. We believe that the simultaneously formed carbon matrix hindered the agglomeration of the lead oxide nanoparticles.

Fig. 7 showed the size distribution histogram measured from the well separated particles obtained from the enlarged TEM images of samples from $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$ ratio of 50:50, 40:60, 30:70 and 90:10, respectively. The average particle sizes slightly changed with the $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$ ratio varied in the range of 50:50 to 10:90. The average sizes of the PbO nanoparticles are 9.0 nm, 11.4 nm, 13.5 nm and 12.4 nm, respectively.

3.5. Electrochemical characterization

To investigate the energy storage properties of the as-prepared PbO@C nanocomposites, a series of electrochemical measurements were performed. Fig. 8 presents the second cycle voltammetric profiles of the PbO@C nanocomposites electrodes from the mixtures with $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$ ratio of 100:0, 90:10, 50:50, at a scan rate of 50 mV s^{-1} between -0.5 V and 2.5 V . Generally, the potential for transforming PbSO_4 into Pb was higher than that of hydrogen production, such as the case for pure PbO electrode (Fig. 8a). However, Fig. 8b and c obviously revealed the hydrogen production processes for the samples made from the 90Pb(NO_3)₂:10starch and 50Pb(NO_3)₂:50starch, other than converting PbSO_4 back to lead in each sample. The present results implied that the presence of carbon (even a very small amount) diminished the hydrogen overpotential [35,36]. Two oxidation peaks appeared in the CV curves of all the tested samples between -0.5 V and 0.8 V . The oxidation processes corresponded to the transformation between Pb and PbSO_4 . The wide current plateau above 0.0 V responds to the formation of lead oxide [37–39].

Fig. 9 shows the first cycle discharge voltage profiles of pure PbO and PbO@C nanocomposites made from the precursors with the $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$ ratio of 100:0, 90:10, 70:30, 50:50, 30:70 and 10:90 at a current density of 400 mA g^{-1} . To the cutoff voltage of 1.0 V , the discharge capacities of PbO@C electrodes with the initial weight ratio $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$ are in the order of $70:30 > 50:50 > 90:10 > 100:0 > 30:70 > 10:90$, moreover, still lower than the theoretical capacity of lead oxide (240 mA h g^{-1}).

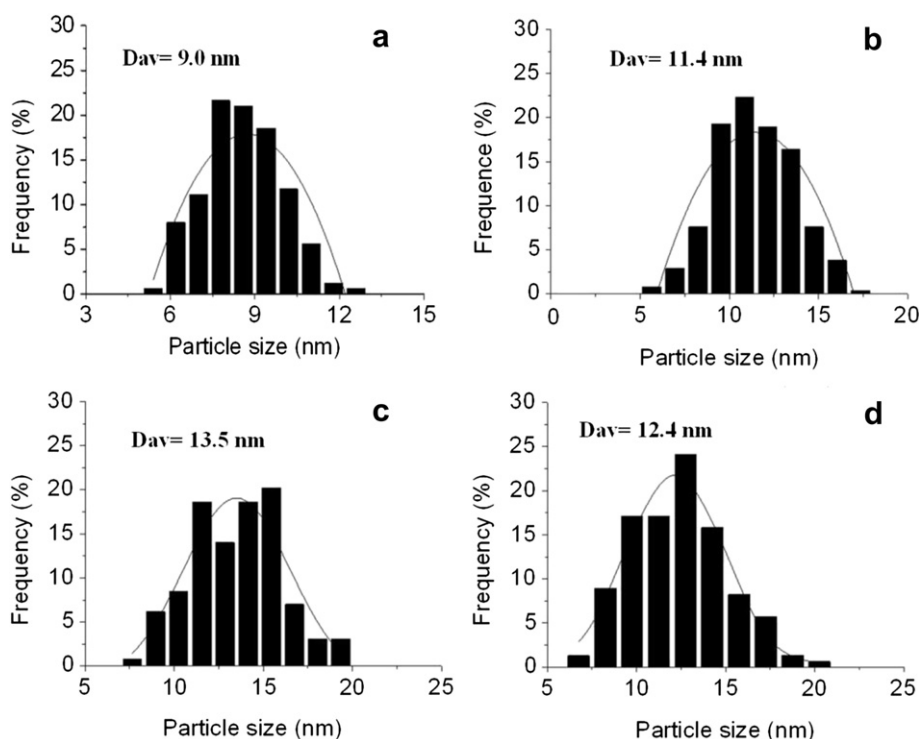


Fig. 7. Histogram of the PbO particle size distribution on the carbon matrix for samples from $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$ ratio of (a) 50:50, (b) 60:40, (c) 70:30 and (d) 90:10.

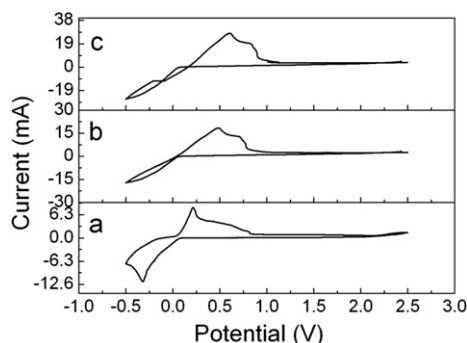


Fig. 8. Cyclic voltammetry (CV) carried out at 50 mV s^{-1} scan rate for PbO@C electrode from $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$ ratio of (a) 100:0, (b) 90:10 and (c) 50:50.

The detected iR drop (ΔV) at the initial stage of discharge increased from 0.1 V to 0.2 V when the carbon content of nanocomposites was increased from 0% to 55.3%. A sudden voltage drop represents the voltage change due to some complex polarization and internal resistance of the battery system. Samples from $30\text{Pb}(\text{NO}_3)_2:70\text{s-tarch}$ and $10\text{Pb}(\text{NO}_3)_2:90\text{s-tarch}$ exhibited the obvious double layer regions between 2.4 and 1.6 V. The double-layer region of other samples was narrow, only between 2.4 and 2.1 V. The voltage plateaus for sample from $90\text{Pb}(\text{NO}_3)_2:10\text{s-tarch}$ appearing at 2.1–2.0 V can be ascribed to the reduction of PbO_2 into PbSO_4 . For sample from $50\text{Pb}(\text{NO}_3)_2:50\text{s-tarch}$, there existed two broadly defined voltage plateaus. The first voltage plateau showing at 2.1–1.9 V also can be ascribed to the reduction of PbO_2 into PbSO_4 . While the second plateau shown at 1.5–1.35 V could be ascribed to the reduction of Pb into PbSO_4 . The open-circuit voltages of all samples are about 2.4 V.

Fig. 10 presents the discharge curves of PbO@C electrode from the precursors of $70\text{Pb}(\text{NO}_3)_2:30\text{s-tarch}$ at different discharge rates. The experimental results clearly indicated that the longest discharge time happened at a current density of 200 mA g^{-1} , corresponding to the discharge rate of 1 C. When the discharge density was elevated to 800 mA g^{-1} , the discharge process completed within only 3 min for the same voltage range. Besides the increased discharge density, the iR drop also plays a certain part on the greatly shortened discharge time. Therefore, the initial abrupt voltage decreasing diminished the usable battery voltage.

Fig. 11 showed the cycle performances of the lead-acid batteries by using the PbO@C nanocomposites as the anode materials at a constant charge/discharge current of 400 mA g^{-1} . Samples from the pure $\text{Pb}(\text{NO}_3)_2$ and $90\text{Pb}(\text{NO}_3)_2:10\text{s-tarch}$ exhibited very close battery properties over 100 charge/discharge cycles. Although a very small

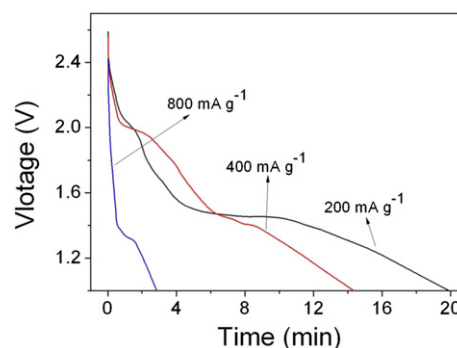


Fig. 10. Discharge behaviors of PbO@C electrode from $70\text{Pb}(\text{NO}_3)_2:30\text{s-tarch}$ at various discharge current densities in H_2SO_4 solution.

amount of carbon was present in the sample from $90\text{Pb}(\text{NO}_3)_2:10\text{s-tarch}$, the initial capacities increased to $141.5 \text{ mA h g}^{-1}$, which is larger than that of pure PbO ($132.2 \text{ mA h g}^{-1}$). After the quick attenuation in the initial 20 cycles, the capacity stabilizes at ca. 95 mA h g^{-1} for the pure PbO and 107 mA h g^{-1} for the sample from $90\text{Pb}(\text{NO}_3)_2:10\text{s-tarch}$. When the starch content was increased to 30 wt.%, the obtained PbO@C nanocomposites exhibited a maximum initial capacity of 205 mA h g^{-1} (85% of the theoretical value for PbO) over 1.0–2.5 V voltage range. Its capacity has an obvious declining tendency, similar to the two samples mentioned above. After 100 charge/discharge cycles, a residual capacity of 158 mA h g^{-1} sustained, which was higher than the initial value of the first two samples. As the starch content further increased to 50 wt.% and 70 wt.%, the initial capacities (185 mA h g^{-1} and 109 mA h g^{-1} , respectively) were comparatively lower. However, the capacities quickly increased after the first cycle. The lessened initial capacities originated from the diffusion limitation of sulfuric acid on the electrode surface. After the capacity increased to 195 mA h g^{-1} in the third cycle, the capacities gradually decayed when using the PbO@C nanocomposites prepared from $50\text{Pb}(\text{NO}_3)_2:50\text{s-tarch}$ as the electrode materials. Despite the lower initial capacity, a highest residual capacity of 174 mA h g^{-1} remained after 100 cycles for the PbO@C nanocomposites prepared from $50\text{Pb}(\text{NO}_3)_2:50\text{s-tarch}$, which was higher than the value reported by Cruz [4]. The PbO@C nanocomposites from the $30\text{Pb}(\text{NO}_3)_2:70\text{s-tarch}$ exhibited the best cyclic stability. Although the initial capacity was as low as 109 mA h g^{-1} , the capacity fluctuated between 143 and 145 mA h g^{-1} after the capacity increased in the initial 20 cycles. The present results implied that introducing carbon in the electrode was beneficial to raise the capacity of lead-acid battery and improve the cycling stability.

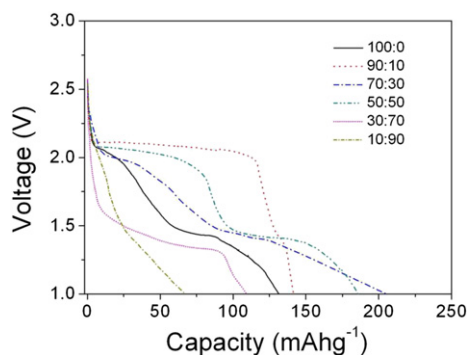


Fig. 9. The first discharge profiles of PbO@C electrode from $[\text{Pb}(\text{NO}_3)_2:\text{starch}]$ ratio. The applied current density is 400 mA g^{-1} .

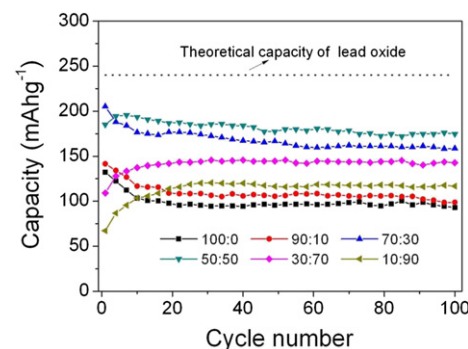


Fig. 11. Charge/discharge cycle performances of the nanostructured PbO and PbO@C nanocomposites as anode materials in the lead-acid battery at a charge/discharge current of 4 mA in the potential range between 1.0 and 2.5 V.

Carbon materials have been widely used as the additive to the anode or cathode in lead-acid battery for years. There have been many speculations about the function of the carbon, but there has never been a universal agreement on the reasons for its use [40,41]. Several possible mechanisms have been proposed to explain the improved properties of the lead-acid batteries by introducing carbon into the electrodes [42–46]. In the present work, the carbon in the nanocomposites acted primarily as a capacitance to increase the capacity of lead-acid battery. The improved specific capacity also originated from considerably increased surface area of the monodispersive nanosized PbO particles in the nanocomposites, which supplied more active sites within the electrolyte. The oxygen-rich groups in the surface of the carbon matrix were also of benefit to increase the capacity [2,47]. The carbon may also serve as a second phase to impede the growth of lead sulfate crystallites and keep the particles apart from each other. Moreover, the improved cyclic stability of the PbO@C nanocomposites was attributed to the ductility of the carbon matrix, which not only acted as a buffer to greatly alleviate the volume changes of PbO particles during the redox reaction in the H₂SO₄ solution, but also inhibited the aggregation of PbO particles into large clusters to enhance the structural stability of the PbO@C anodes [48,49].

4. Conclusions

In a summary, a facile method was developed to prepare PbO@C nanocomposites by pyrolyzing Pb(NO₃)₂ impregnated starch gel based on the coordination chemistry. The products contained nearly monodispersed PbO nanoparticles that homogeneously embedded in the carbon matrix. The particle sizes were ca. 10 nm and slightly changed with the [Pb(NO₃)₂:starch] ratio varied in the range from 50:50 to 10:90. The embedded PbO in the nanocomposites were mixtures of α -PbO and β -PbO. A large amount of Pb formed due to the reduction by excess of carbon. When used as anode materials for lead-acid battery, the presence of carbon enhanced the battery performances. Pb@C nanocomposites prepared from the mixtures with [Pb(NO₃)₂:starch] of 70:30, 50:50 and 30:70 exhibited the highest capacity of 205 mA h g⁻¹, the highest residual capacity of 185 mA h g⁻¹ and the best cyclic stability after 100 charge/discharge cycles, respectively. The present results implied that the PbO@C nanocomposites prepared by our new route were promising electrode candidates for lead acid batteries.

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